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Lattice variation and thermal parameters of KDP crystals added with urea and $NiSO_4.7H_2O$

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Abstract Pure and impurity added (with urea and $NiSO_4.7H_2O$) KDP single crystals were grown by the slow evaporation method from aqueous solutions. Density was measured by the floatation method. X-ray diffraction data were collected for powder samples and used for the estimation of lattice variation and thermal parameters like Debye-Waller factor, mean - square amplitude of vibration, Debye temperature and Debye frequency. No serious lattice distortion was observed due to impurity addition. The thermal parameters do not vary in a particular order with respect to impurity concentration. The results obtained are reported.

Keywords Impurity added KDP crystals, X-ray diffraction analysis, lattice parameters

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1. Introduction

The Debye temperature is derivable from experimental data like specific heats, elastic constants, X-ray and neutron diffraction intensities, *etc*. It is possible to estimate the Debye temperature from the data like melting points, compressibility and microhardness by the uses of semi-empirical relations [1]. But the values obtained from them are not that much accurate as those from specific heats or elastic constants. These relations have been tested on pure crystals as well as (cubic) mixed crystals. Various methods of determination of Debye temperatures have been discussed in reviews by Blackman [2], Herbstein [3], Mitra [4] and Alers [5]. An efficient method of determining the Debye temperature is from the Debye-Waller factor obtained from X-ray (powder or single crystal) diffraction data [6, 7]. By using this method, the Debye temperatures have been estimated for mixed crystals like $AgCl_xBr_{1-x}$ [8] and alkali halide mixed crystals [7, 9-13]. As this method is suitable for any crystal system, this method can be adopted for pure and impurity added crystals of potassium dihydrogen orthophosphate (abbreviated as KDP).

KDP (KH_2PO_4) belongs to the scalenohedral (twelve sided polyhedron) class of tetragonal crystal system and has created considerable interest among several research workers. It has a tetramolecular unit cell having the dimensions [14] given as $a = b = 7.448$ Å and $c = 6.977$ Å. It is soluble in water and the molecular weight and density are 136.09 and 2.338 g/cc respectively [15]. Pure and impurity added KDP crystals were grown from aqueous solutions and also in gel media by different workers [16-20].

A research programme on the growth and physical properties of pure and impurity added KDP crystals is on hand in this laboratory. As a part of the programme, lattice parameters, Debye-Waller factors, Debye temperatures and Debye frequencies have been determined from X-ray diffraction data for pure and two impurity added KDP systems. Urea (N_2H_4CO, an organo non-linear optical material having small molecular size than KDP and no common ion with KDP) and nickel sulphate heptahydrate ($NiSO_4.7H_2O$, a transition metal compound having large molecular size and less density than KDP and no common ion with KDP) are the two impurities (added in the solution used for the growth of single crystals with impurity concentration in the range of 2000 to 10000 ppm, *i.e.* 0.2 to 1.0 mole %) considered in the present study. We report here the results obtained in our study.

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2. Experimental

Analytical reagent grade (AR) samples of KH_2PO_4, urea and $NiSO_4.7H_2O$ along with double distilled water were used for the growth of single crystals by slow evaporation method. KDP was added with urea and $NiSO_4.7H_2O$ separately each in six different KDP : impurity molecular ratios, *viz.* 1:0.000 (pure KDP), 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010. The impurity was dissolved in 2.5 M solution of KDP. Supersaturated aqueous solution of the salt (2.5 M) was prepared in a 100 ml beaker (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition. The temperature and volume were kept constant respectively at 30°C and 25 ml for all the crystal growth experiments. Small crystals appeared in the beginning due to slow evaporation and grew larger in considerable finite time. Best crystals were selected from this and used for the measurements.

Densities of the grown crystals were measured by the floatation method. It was observed that the difference in densities of crystals grown in the same container was very small and negligible.

X-ray diffraction data were collected from powder samples of crystals using an automated X-ray diffractometer with monochromated CuK_α radiation (λ = 1.54256Å) and scintillation counter (scan speed 2°/min) at a temperature of 25°C ± 1°C (2θ range : 10 to 90°). The reflections were indexed following the procedures of Lipson and Steeple [21]. Processing of the raw intensity data was done following the procedures of Warren [22]. Lattice parameters were determined from the indexed data using high angle reflections.

The mean Debye-Waller factors (B) were determined by the Wilson plot method [23]. For the calculation of structure factors, the atomic scattering factors were taken from the literature [24,25]. For pure KDP crystal, the structure factor is :

$$F = 4f_K + 8f_H + 4f_P + 16f_O = F_{KDP}.$$

The density measurement shows qualitatively that the impurity molecules have entered into the KDP lattice. Moreover, the impurity concentration considered in the present study are small. So, for impurity added KDP crystals, the impurity molecules are assumed to be added in the KDP lattice in the same ratio taken in the solution used for the growth of single crystals. Hence for impurity added KDP crystals, the structure factors are :

$$F = F_{KDP} + P(4f_C + 4f_O + 8f_N + 16f_H)$$

for urea added KDP crystals ; and

$$F = F_{KDP} + P(4f_{Ni} + 4f_s + 44f_O + 56f_H)$$

for $NiSO_4.7H_2O$ added KDP crystals. P is having the values 0.002, 0.004, 0.006, 0.008 and 0.010 respectively for the KDP : impurity molecular ratios 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010.

From the Debye-Waller theory

$$B = (6h^2 / mkT)\, W(x),$$

where m is the mean atomic mass, T the absolute temperature at which the intensities are measured and h and k the Planck's and Boltzmann's constants respectively. The function $W(x)$ is given by

$$W(x) = \left[\varphi(x) / x^2\right] + (1/4x),$$

where $x = (\theta_D / T)$ and $\varphi(x)$ is an integral. The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill [26]. From the above relations, Debye temperatures (θ_D) can be evaluated. The mean square amplitude of vibration ($\overline{u}^2$) can be obtained from [27] as

$$B = 8\pi^2 \overline{u}^2.$$

The Debye frequency (f_D) can be obtained from [28] as

$$\theta_D = f_D(h/k).$$

3. Results and discussion

All crystals grown in the present study were found to have the scalenohedral morphology as that for pure KDP crystals. All the grown crystals were found to be stable. $NiSO_4.7H_2O$ added KDP crystals were light greenish in colour.

Intensity of green colouration increased with the increase in impurity concentration showing that the $NiSO_4.7H_2O$ molecules have entered into the KDP lattice. Urea added KDP crystals were transparent.

The densities are given in Table 1. The density measured for the pure KDP in the present study compares well with the

Table 1. Lattice parameters (a and c), volumes and densities of pure and impurity added KDP crystals.

System (Impurity in mole %)	a(Å)	c(Å)	Volume (Å³)	Density (g/cc)
a) Pure KDP	7.4533	6.9913	388.4	2.34
b) Urea added KDP				
0.2	7.4697	6.9815	389.5	2.32
0.4	7.4362	7.0657	390.7	2.31
0.6	7.4813	7.0004	391.8	2.28
0.8	7.5147	6.9590	392.9	2.26
1.0	7.4831	7.0311	393.7	2.24
c) $NiSO_4.7H_2O$ added KDP				
0.2	7.4773	7.0382	393.5	2.33
0.4	7.4575	7.0963	394.7	2.32
0.6	7.4999	7.0373	395.8	2.31
0.8	7.4838	7.0800	396.5	2.30
1.0	7.4964	7.0716	397.4	2.28

reported in the literatrue [15]. For both the impurities considered in the present study, the observed decrease of density of KDP crystal caused by the impurities indicates that the impurities have entered into the lattice of KDP crystals. Moreover, it can be seen that the density decreases further with the increase in impurity concentration of the aqueous solution of KDP used for the growth of crystals.

Calculation of $\Delta 2\theta$ values ($\Delta 2\theta = 2\theta_{exp} - 2\theta_{calc}$; $2\theta_{exp}$ is the experimentally observed 2θ value and $2\theta_{calc}$ is the 2θ value calculated using the lattice parameters for pure KDP crystal available in the literature [14] was done to check for any serious lattice distortion. The $\Delta 2\theta$ values vary from – 1.764 to + 1.656 suggesting that the structures are slightly distorted compared to the structure reported earlier [14]. This may be attributed to strains caused by powdering the sample crystals as well as the addition of impurities. Large deviations are not observed (to have any serious lattice distortion) in any of the samples studied in the present work.

Lattice parameters obtained (a and c) and volume are presented in Table 1. The lattice volume (V) of the impurity added KDP crystals increases with the increase in impurity concentration. This also shows that the impurity molecules have entered into the KDP lattice. The lattice parameters obtained for pure KDP compare well with those reported in the literature [14].

Values of B, $\bar{u}^2$, θ_D and f_D are presented in Table 2. No particular order was observed in the case of thermal parameters obtained, *viz.* B, $\bar{u}^2$, θ_D and f_D with respect to impurity concentration. No comparison is made with other studies since there is no data available in the literature for the systems considered in the present study.

Table 2. Thermal parameters of pure and impurity added KDP crystals

System (Impurity in mole %)	B(Å^2)	$\bar{u}^2$(Å^2)	θ_D(K)	$f_D \times 10^{12}$ (s^{-1})
i) Pure KDP	7 151	0 091	168 5	3 512
ii) Urea added KDP				
0 2	7.745	0.098	161.9	3.373
0 4	6 354	0 080	179.1	3 732
0 6	6.620	0.084	175 5	3 657
0 8	6 277	0 079	180 4	3.759
1 0	7.919	0 100	160.5	3.344
iii) $NiSO_4.7H_2O$ added KDP				
0 2	5 568	0.071	191.5	3 988
0 4	7.662	0.097	163.2	3.399
0 6	6.403	0 081	178.9	3.726
0 8	8.585	0.109	154.5	3.218
1.0	5.544	0.070	192 9	4.018

The Debye frequencies observed in the present study lie in the infrared range and that for the pure KDP (3.512×10^{12} s^{-1} at 25°C) nearly coincides with the frequency of v mode (2.5×10^{12} s^{-1} at 27°C) [29] assigned to oscillation modes of protons. This is one order of magnitude lower than that obtained by O'Keeffe and Perrino (3×10^{13} s^{-1}) [29, 30] for the proton jump frequency and that found (4×10^{13} s^{-1}) [29] for oscillation frequencies of the P-O-H group in orthophosphates.

4. Conclusion

Pure and impurity added (with urea and $NiSO_4.7H_2O$) KDP single crystals were grown from aqueous solutions and X-ray powder diffraction analyses were done. The obtained thermal parameters do not follow any particular order with respect to impurity concentration.

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